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A Technical Demonstration of the Initial Stage of Mo-99 Recovery from a Low Enriched Uranium Sulfate Solution

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Previous LANL Based Separation Chemistry Research in Support of SHINE Medical Technologies Inc.

- **Experimental work started January 2011**
- **Focus on the initial separation and recovery of Mo-99 from aqueous uranium solutions – the target for particle accelerator produced Mo-99**
- **Multiple LEU Sample Irradiations**
  - Evolving sample containment and sample irradiation capability
  - Demonstrated that Mo-99 can be recovered in > 90% yield from irradiated uranium solutions using titania as a sorbent
  - Demonstrated that Mo-99 can be recovered from both irradiated uranium sulfate and nitrate solutions
  - Uranium sulfate - potential operational advantages *vs.* uranium nitrate fuel

Dale, G.E., Dalmas, D.A., Gallegos, M.J., Jackman, K.R., Kelsey, C.T., May, I., Reilly, S.D., Stange, G.M., "Mo-99 Separation from High Concentration Irradiated Uranium Nitrate and Uranium Sulfate Solutions." Ind. Eng. Chem. Res. (2012) 51:13319-13322.

Technical Challenge

- **Confirm high % Mo-99 recovery from irradiated uranyl sulfate using a direct downscale of a titania column recovery process that could be used in plant operations**
- **Confirm the fuel recycle concept – irradiated uranyl sulfate can be recycled with no loss in % Mo-99 recovery**

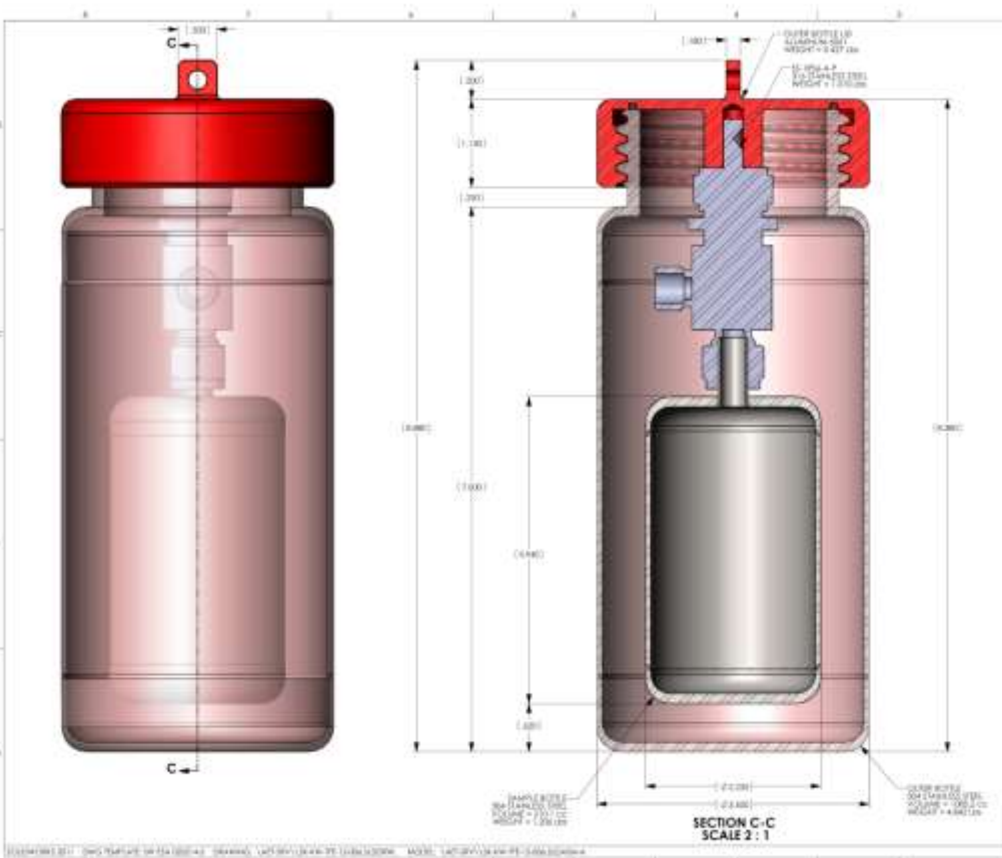
- ***Requires design of new sample containers for containment of greater volumes of solution (up to 150 mL)***
- ***Requires access to a new capability for sourcing neutrons at LANSCE (Target 4)***
- ***Requires new procedures for LEU uranium and irradiated sample chemical manipulations***
- ***Requires the development of semi-automated column separation apparatus that can ultimately be used in a hot cell***

Uranium Sulfate Fuel Preparation

- **Started with 19.5 % ^{235}U enriched uranium nitrate solution**
- **Converted to uranium sulfate solution using standard inorganic chemical procedures**
  - removing all the nitrate a non-trivial task
- **Final uranium fuel concentration – aimed for 150 gU/L (0.63 mol/L)**
  - 150.4 gU/L using 'in house' developed spectroscopic technique
  - 150.3 gU/L by Davies-Gray titration
- **Prior to sample irradiation fuel spiked with aqueous solution of Na_2MoO_4 (sodium molybdate) to more accurately reflect Mo-99 production concentration**

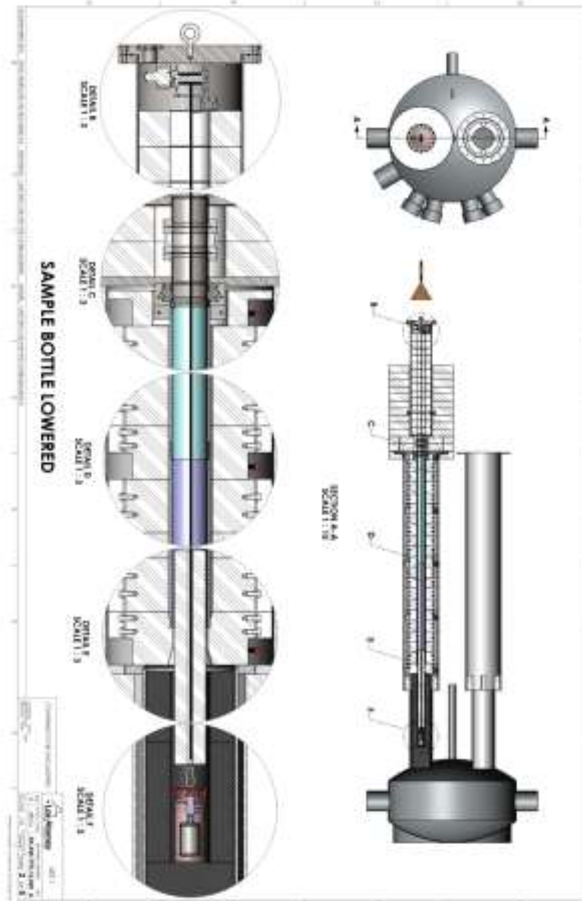
Technique development – major contribution from University of Wisconsin summer students Gary Stange and Alex Schroeder

Sample Containment for Irradiation



Target 4 – Capability Development

- **New irradiations capability at LANSCE**
- **“90 Up” flight path**
- **10^9 n/cm^2/sec thermal neutron flux**
- **Performed 3 sample irradiations and Mo-99 separation chemistry between December 2012 and January 2013**
- **Shipped solutions to TA-48 for separation chemistry experiments**



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Target 4 – Capability Development

Irradiated Sample – Gas Collection for Later Analysis

- Samples degassed (freeze-pump-thaw) before irradiation to minimize background from air
- Irradiated samples placed under argon atmosphere (~600 Torr)
- After irradiation, head space gas (~60 cc) expanded into evacuated cylinder (500 cc) and stored to decay
- Analysis by mass spectrometry in progress (H_2 & O_2)

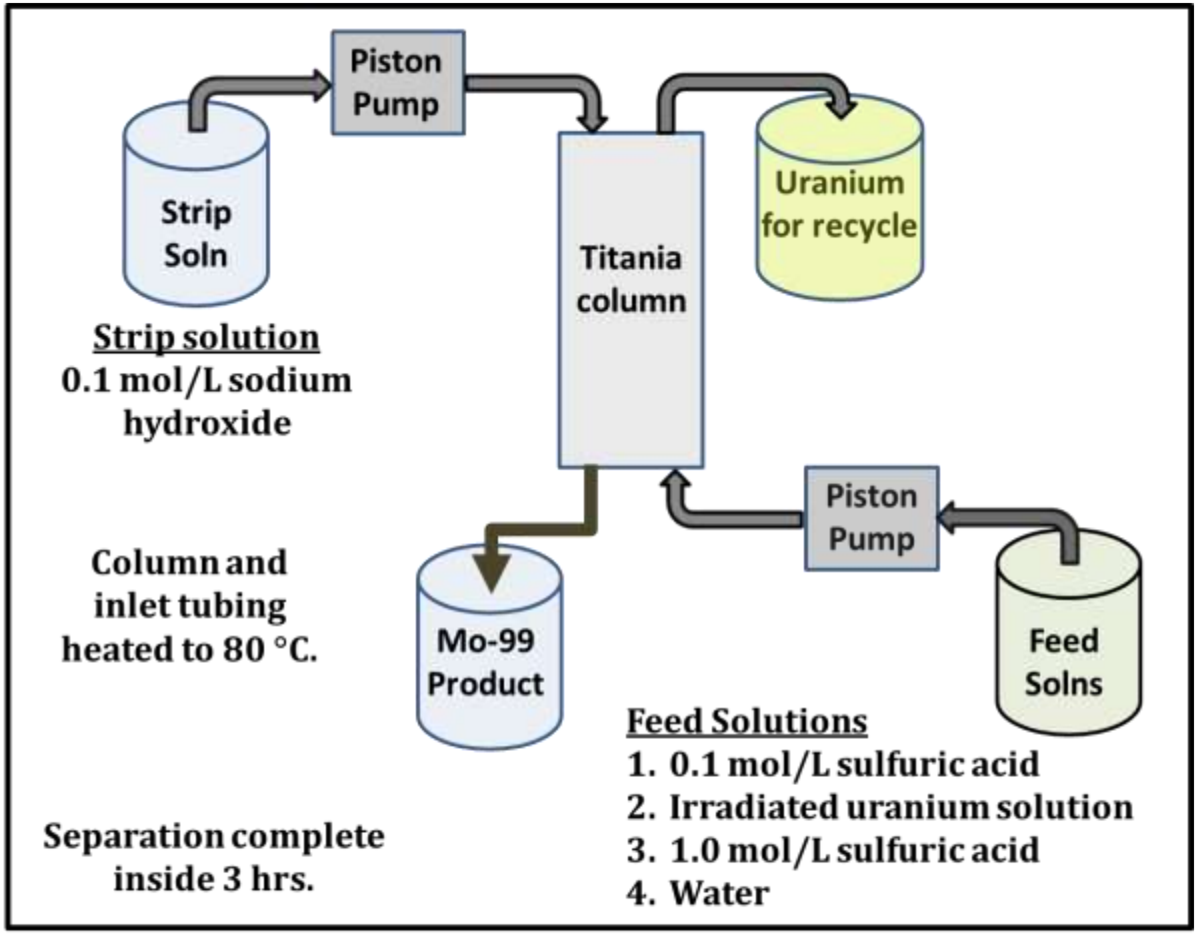
Irradiated LEU Solutions – Experimental Details

Experimental Details	1st Irradiation	2nd Irradiation	3rd Irradiation
Irradiation date	11th Dec. '12	9th Jan. '13	28th Jan. '13
Uranium conc. (mol/L)	0.63	0.65	0.64
Solution density (g/mL)	1.19	1.20	1.21
% recycle irradiated uranium	0 %	78 %	77 %
pH before irradiation	1.0	1.2	1.1
pH after irradiation	1.1	1.2	1.2
Mo-99 production (µCi)	1000	900	1100

DIRECT DOWNSCALE OF SHINE COLUMN PROCESS

- **Titania column designed to separate Mo-99 from the vast excess of LEU in dilute sulfuric acid solution**
  - Mo-99 product for further downstream processing
  - LEU product for potential recycle
- **Input parameters provided by D. Stepinski, M. Youker & G. Vandegrift at ANL**
  - Based on experimental work and VERSE code simulation
- **Experimental set-up designed by F. Stephens at LANL**
  - Initially designed for fume hood work (TARGET 4 irradiated samples)
  - Must be compatible with hot cell operations
  - Only minor experimental modifications of original input parameters

Schematic of Column Separation



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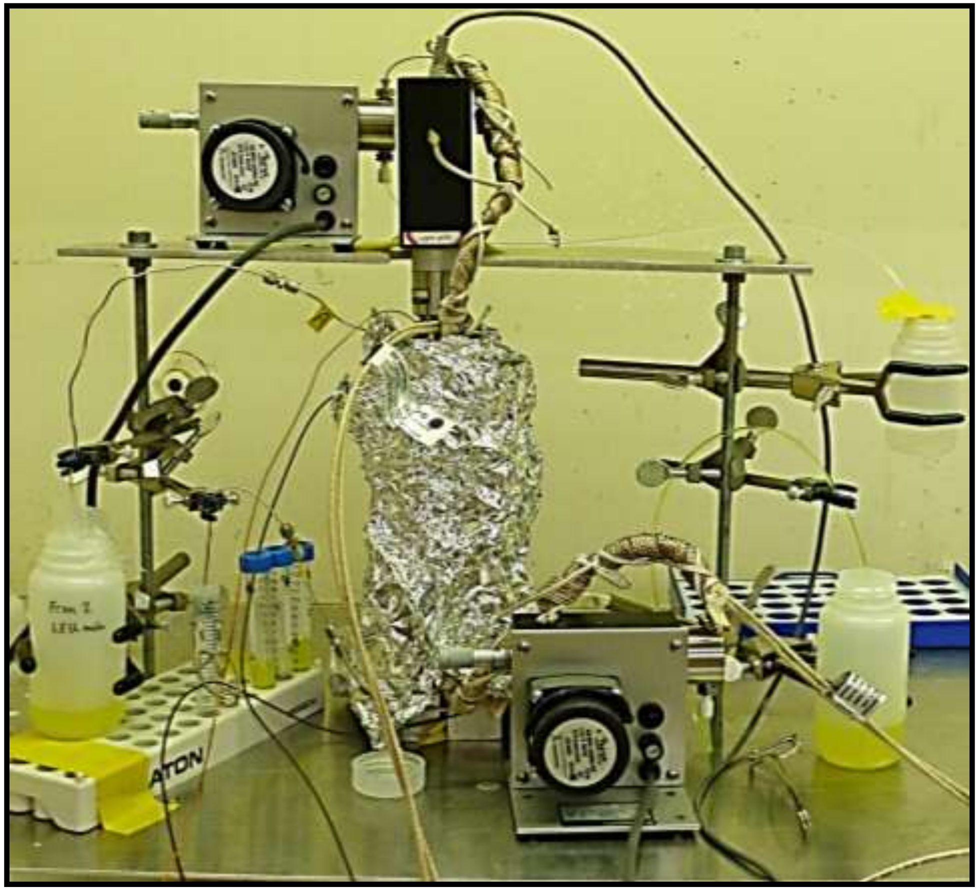
Column Separation Apparatus



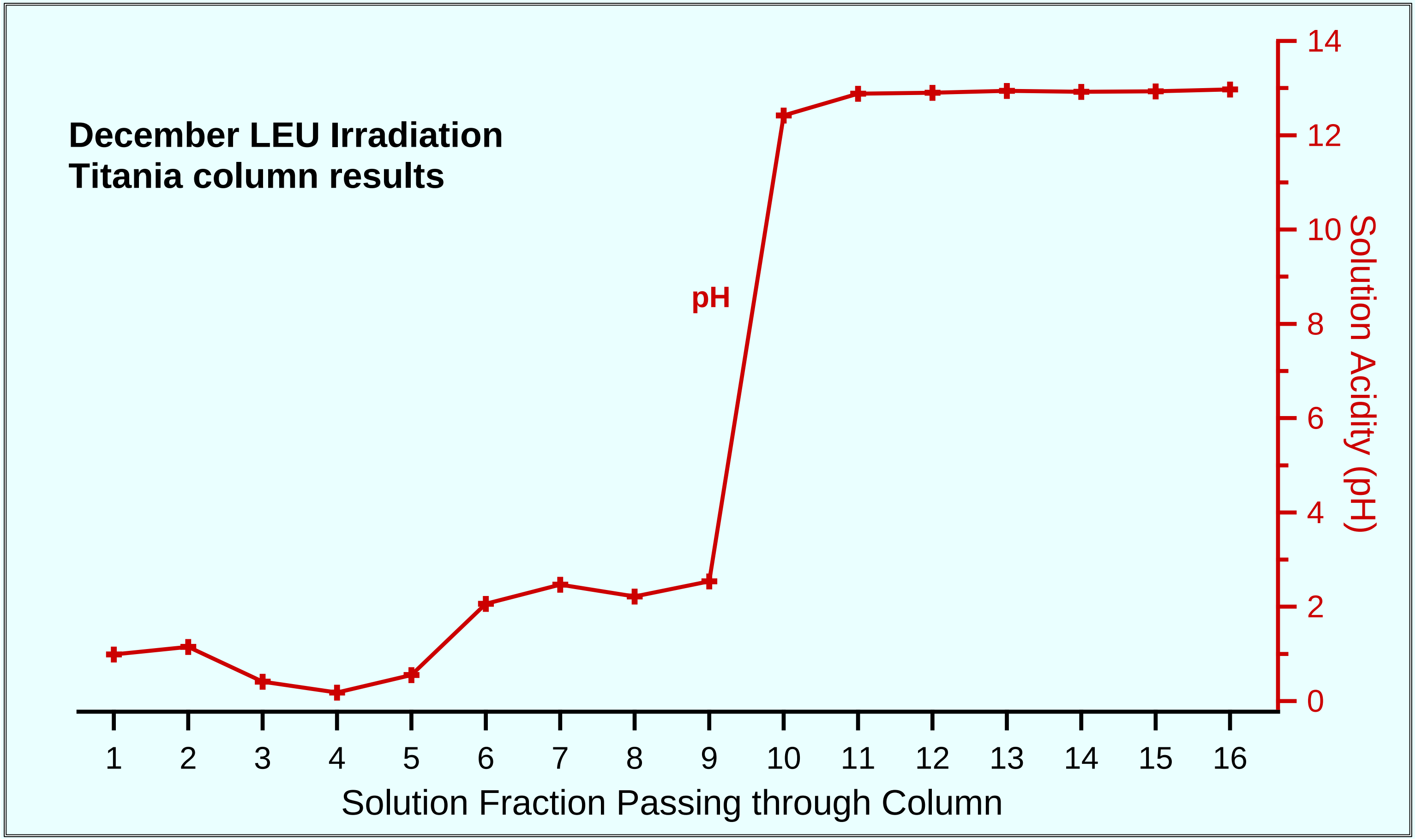
Column and post-experiment titania resin

Direct Downscale Demonstration of Mo-99 Recovery using Titania Column

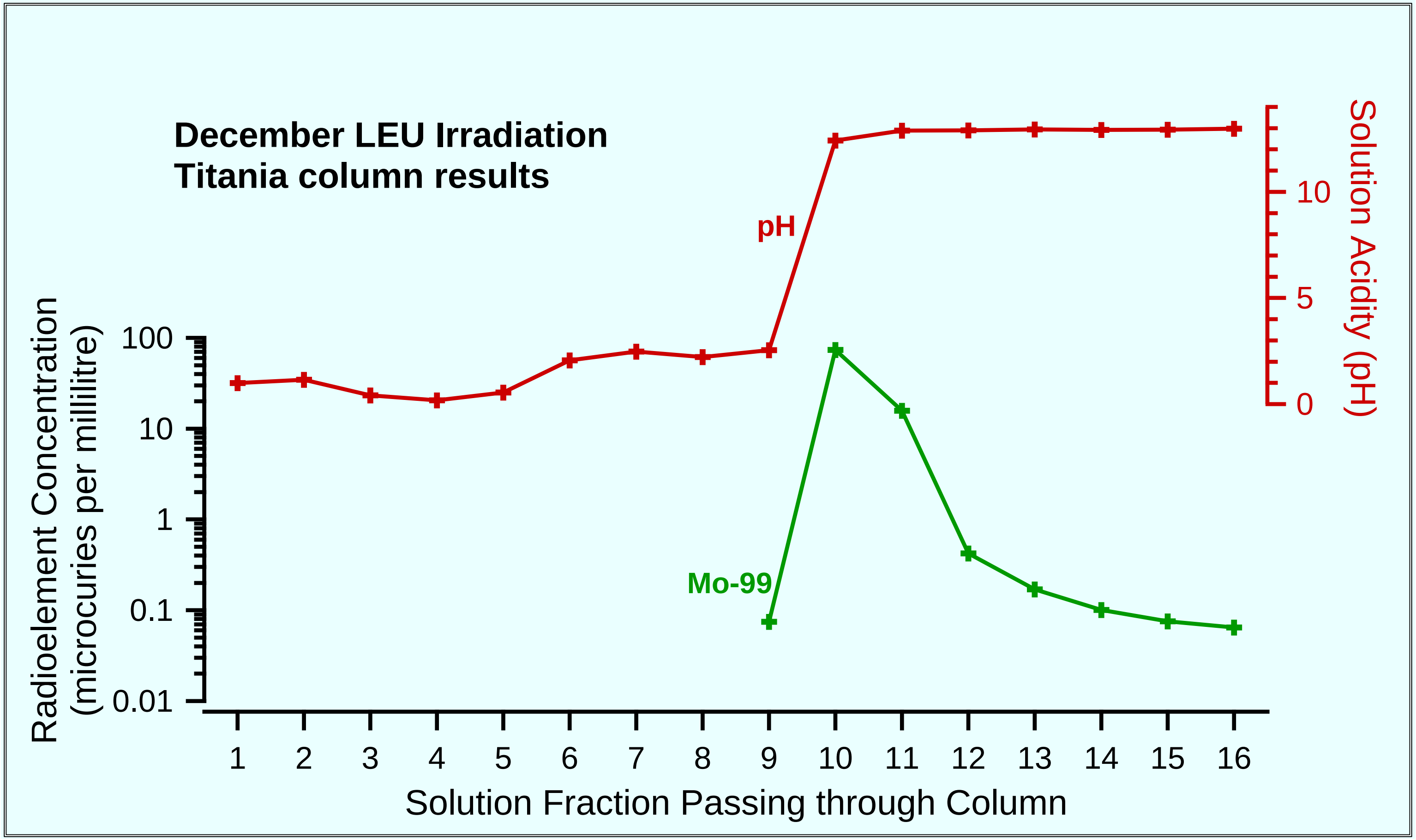
Titania column separation	1st Irradiation	2nd Irradiation	3rd Irradiation
Volume of LEU sulfate feed (mL)	129	128	136
Volume of NaOH strip required for > 95 % Mo-99 recovery (mL)	9.3	9.7	22.3
Mo-99 activity balance (%)	97	102	95

High volume of NaOH strip in 3rd irradiation column separation – attributed to process development for hot cell operation

Titania Separation – Fraction analysis



Titania Separation – Fraction analysis



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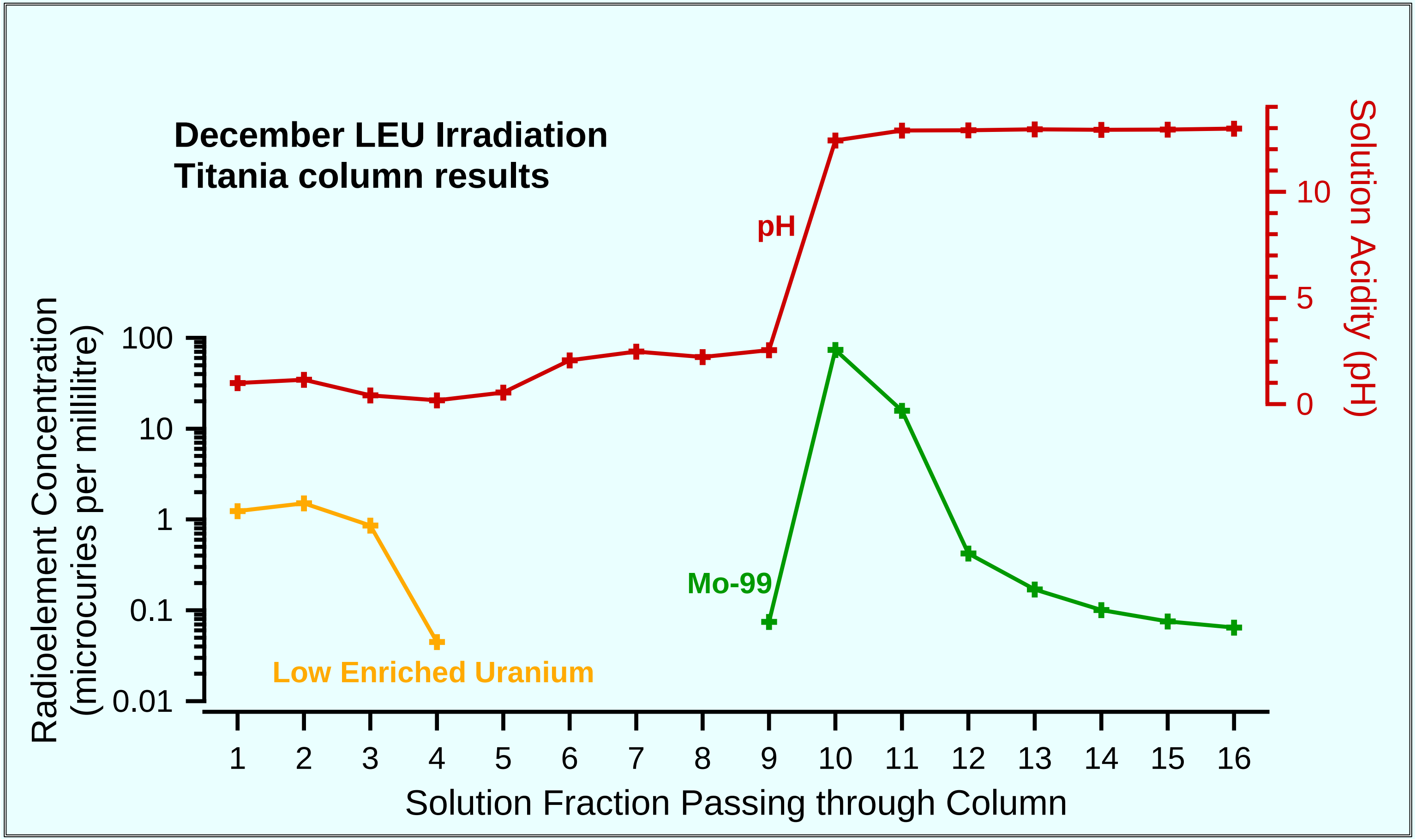
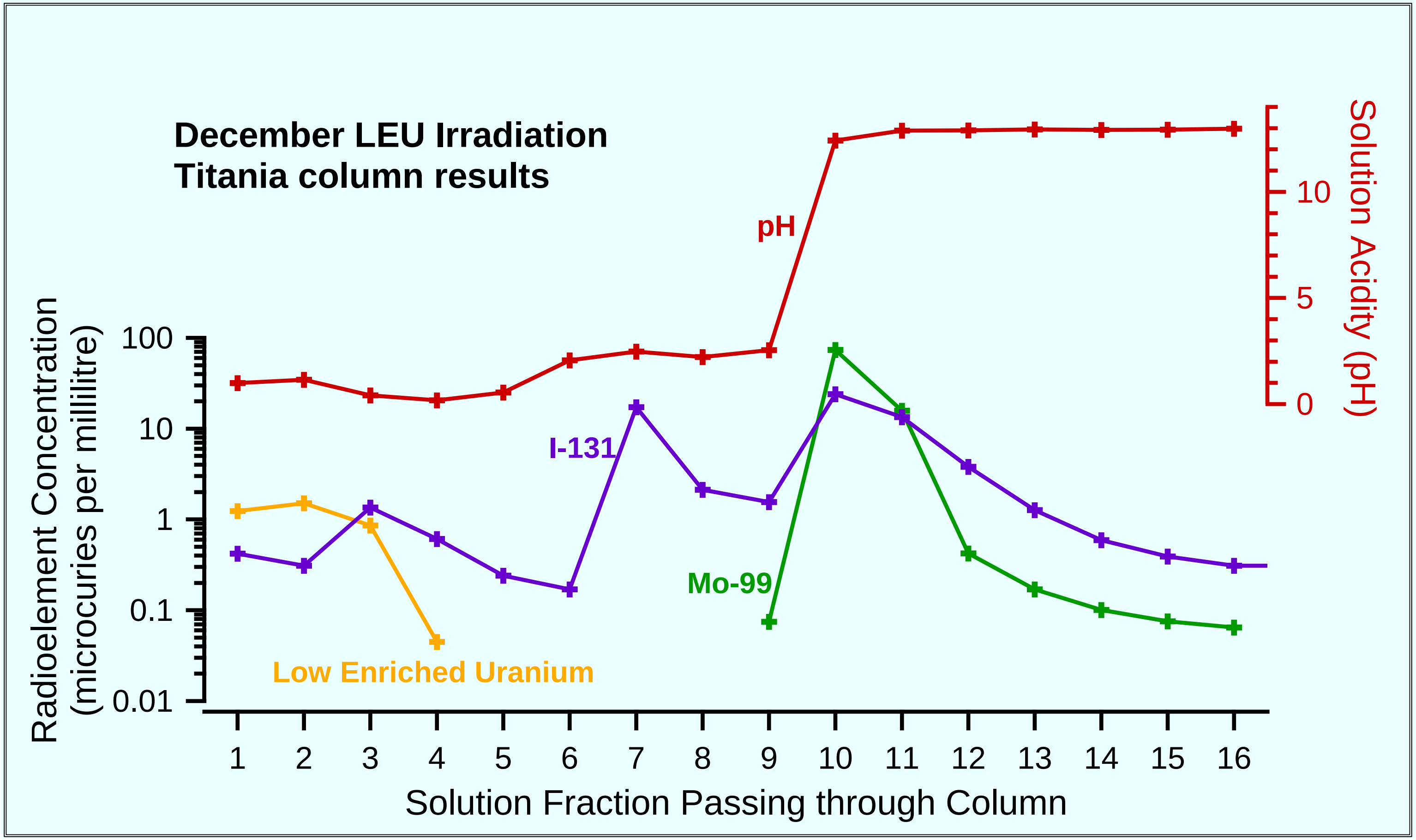


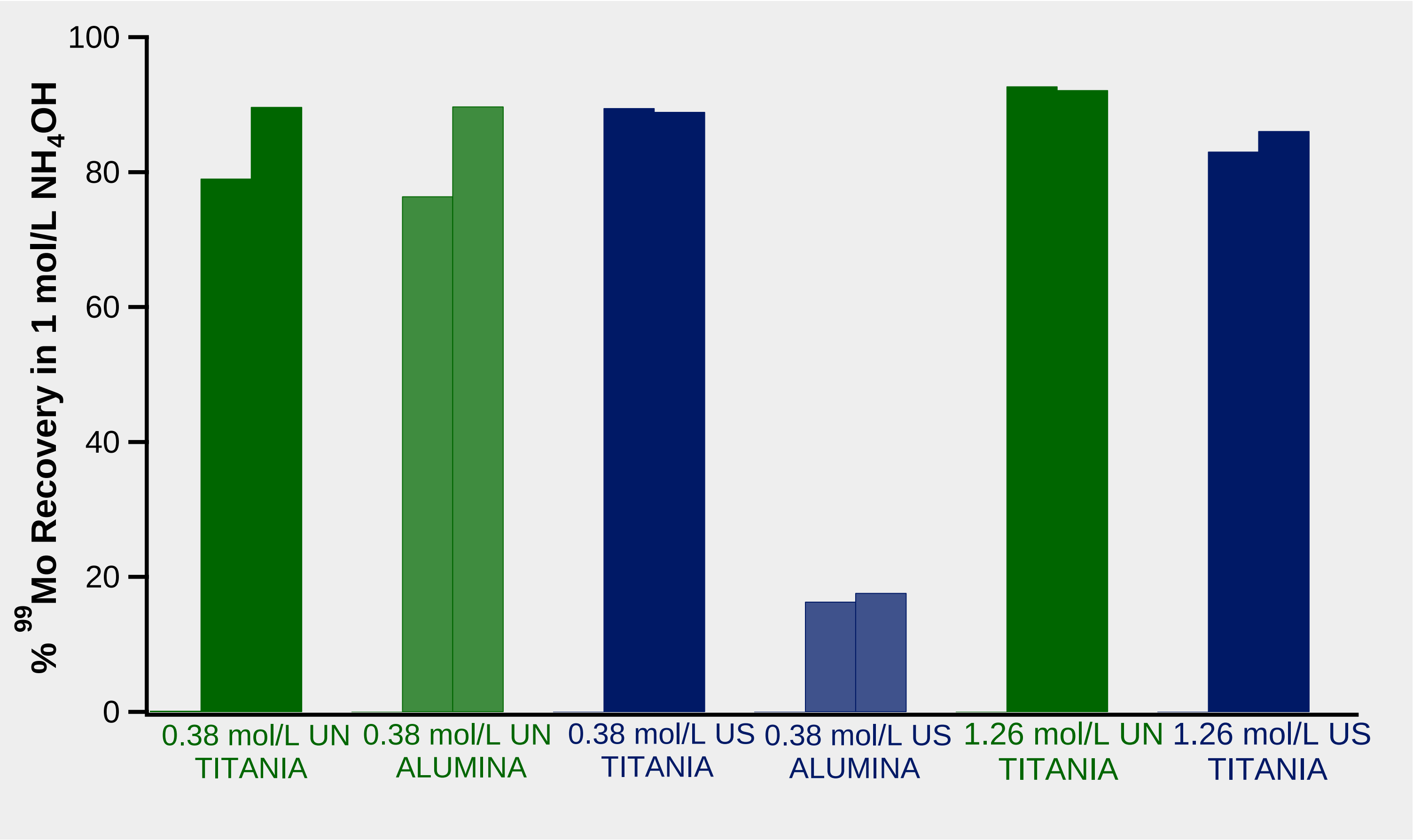
Titania Separation – Fraction analysis



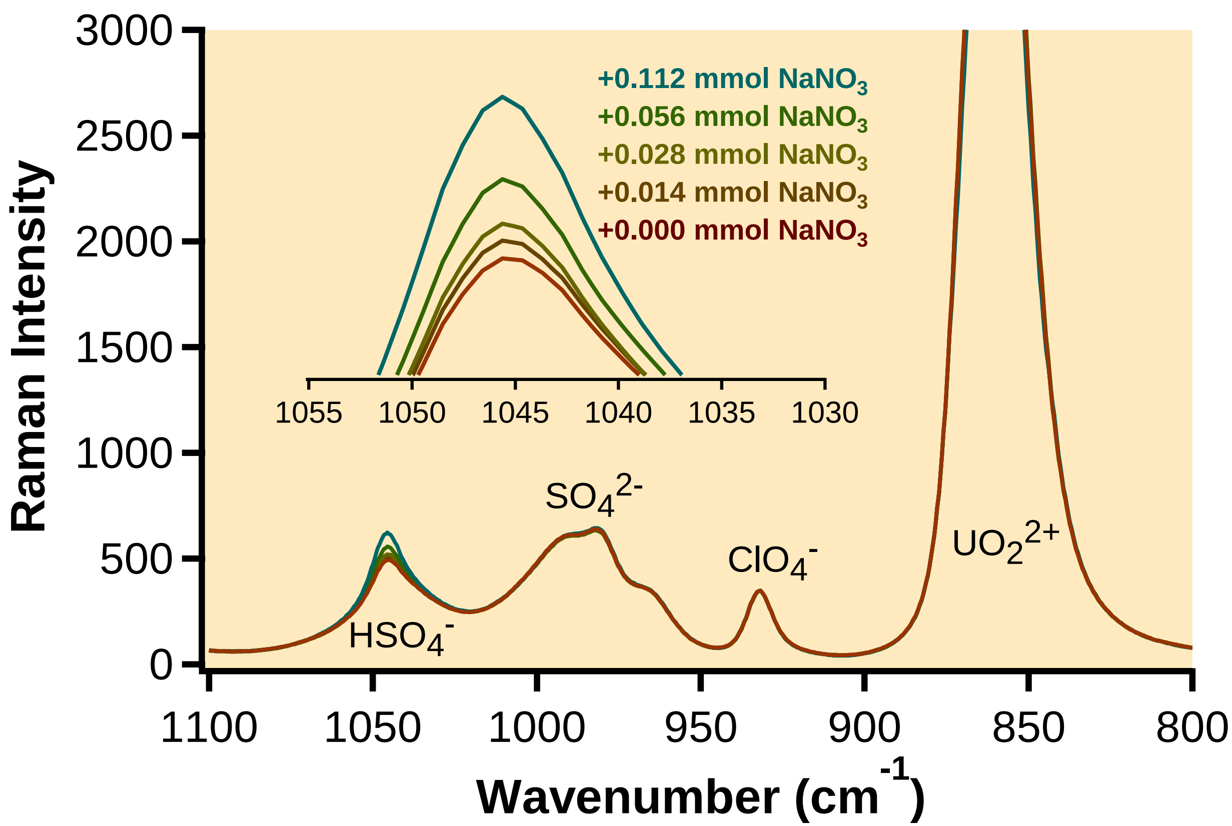
Summary

- New sample irradiation capability (Target 4) and sample containment methods developed
- Well characterized LEU uranyl sulfate fuel prepared
- Fume hood and hot cell compatible separations apparatus developed for downscale testing of titania column recovery of fission Mo-99
- Near quantitative recovery of Mo-99 achieved from irradiated LEU uranium sulfate solutions
- Recycling irradiated LEU uranyl sulfate solutions has no impact on Mo-99 recovery using titania

Previous Batch Distribution Experiments – Jan. 2012
Irradiated uranyl nitrate (UN) and uranyl sulfate (US)

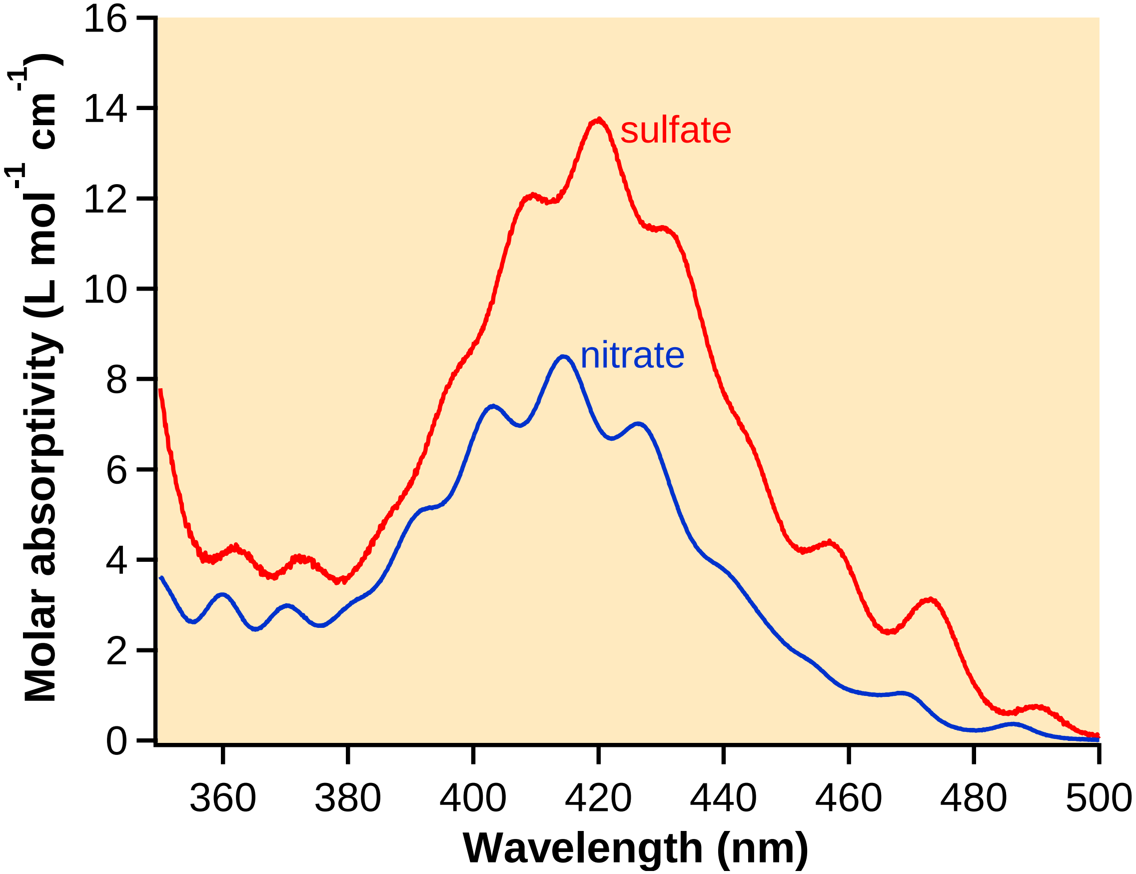


Uranium Sulfate Fuel Preparation
Raman spectra – monitor nitrate removal from sulfate fuel



Technique development – major contribution from University of Wisconsin summer student Gary Stange

Uranium Sulfate Fuel Preparation
UV/Vis technique - determination of uranium concentration



Technique development – major contribution from University of Wisconsin summer student Alex Schroeder

Sample Containment

- Stainless steel outer and inner containers - design provides for double containment of the solution
- The outer bottle is designed to fit within a Viking container for transportation to TA-48
- Outer bottle also filled with 500 mL of water for neutron moderation and a little bit of fission energy absorption.
- EPDM (ethylene propylene diene monomer) o-ring on the outer bottle lid, 100-200 kGy tolerance.
- UHMWPE (Ultra-high-molecular-weight polyethylene) in the valve packing, 1,000 kGy tolerance.
- Inner bottle design pressure is 150 psi & outer bottle design pressure is 25 psi

Tolerance levels from the Nordion Gamma Compatible Materials Reference Guide.

Titania Column Separation

- More detailed analysis of Mo-99 base fractions on going (*e.g.* activities of longer lived radioisotopes such as Ru-103)
- Major contaminants in recycled uranium included Ru-103, I-131, Ba-140, La-140 & Ce-143
- Major contaminants irreversibly bound to the resin included Zr-95/97 and Te-132

Preliminary I-131 Speciation Results (3rd Irradiation)

Sample	IO_3^- (%)	I_2 (%)	I^- (%)	Activity balance (%)
Irradiated solution (3 days after EOB)	48	16	36	76
Irradiated solution (8 days after EOB)	40	23	37	65
Column fraction 2 (irradiated uranium)	25	60	15	70
Column fraction 7 (pH 2.77)	5	67	28	69
Column fraction 9 (11.65)	0	13	87	75